

## *Hydrogen-Abstraction Dynamics Probed with Synchrotron Radiation*

**C**rossed-molecular-beam scattering is at the forefront of experimental means of investigating the fundamental reactive encounters in metathesis reactions, in which a single atom is transferred from a stable molecule to an atom or radical. Berkeley Lab researchers are exploiting a unique combination of intense, tunable VUV synchrotron radiation with the crossed-beam technique on Beamline 9.0.2 at the Advanced Light Source (ALS) to yield important new insights into the dynamics of hydrogen transfer (abstraction) when chlorine reacts with the saturated hydrocarbons pentane and propane.

Metathesis reactions are the only truly bimolecular (i.e., bimolecular in both directions) gas-phase reactions. Those reactions involving hydrogen-atom transfer arguably represent the most important subclass of the vast body of reactions. Free-radical abstractions of hydrogen atoms in saturated hydrocarbons, for example, are reactions of great importance in combustion, and the differing propensities for

reaction of primary, secondary, or tertiary hydrogen atoms, as well as the different dynamics underlying these pathways, are central to a detailed understanding of combustion chemistry. These processes have come under increasing scrutiny in recent years as experimental innovations have allowed more direct probing of the dynamics.

The researchers at the ALS have used the crossed-beam method with a tunable, VUV probe to measure global scattering distributions for reaction of chlorine atoms with saturated hydrocarbons. These measurements provide extremely detailed information about these reactions, allowing answers to questions such as: What are the initial products of the reaction? Where does the energy of the reaction go? Are the products cold (energy mainly in translational motion) or hot (energy mainly in vibrations) or some of each? The use of tunable undulator radiation provides the unprecedented ability to probe the reactive hydrocarbon radical fragment directly in these reactions.

Initial studies of the reaction of chlorine with propane suggested different dynamics for the forward- and backward-scattered products. The researchers have now extended these studies to the reaction of chlorine with n-pentane,  $\text{Cl} + \text{n-C}_5\text{H}_{12} \rightarrow \text{HCl} + \text{C}_5\text{H}_{11}$ , to examine the underlying trends in the dynamics with an eye to the role of the extended carbon skeleton in these reactions.

The experimental results show that the forward-scattered products are clearly associated with the formation of the lowest energy 2-pentyl radicals, while the backscattered products arise from close collisions preferentially involving the terminal carbons to produce 1-pentyl radicals. The forward-scattered products are formed extremely cold and with velocities largely beyond the limit for production of the 1-pentyl radicals. This indicates a "stripping"-type mechanism and a loose transition state for this component of the reaction. For the backscattered products, however, virtually all of the energy of the collision is de-

posited into the 2-pentyl radicals, producing extremely hot, reactive products. This is very different from what was observed in other related systems. In fact, previous studies relying on state-resolved laser probing of the HCl have often assumed that no energy is deposited into vibration of the radical product. These ALS results clearly show that this assumption is incorrect.

Moreover, a dramatic difference observed in the dynamics of the backscattered channel for pentane as compared to propane, the researchers believe, arises from the presence of the extended carbon chain and the larger density of states for the pentane reaction. Estimates show that the 20-femtosecond time scale of the collision is very close to a half-period of the bending vibrations of the carbon backbone, making energy transfer from the collision to the C-C-C bends very efficient. These insights help build the foundation for developing accurate computer models of practical combustion systems.

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D. A. Blank, N. Hemmi, A. G. Suits, and Y. T. Lee, "A Crossed Molecular Beam Investigation of the Reaction  $\text{Cl} + \text{Propane} \rightarrow \text{HCl} + \text{C}_3\text{H}_7$  Using VUV Synchrotron Radiation as a Product Probe," *Chem. Phys.* **231** (1998) 261; N. Hemmi and A. G. Suits, "The Dynamics of Hydrogen Abstraction Reactions: Crossed Beam Reaction  $\text{Cl} + \text{n-C}_5\text{H}_{12} \rightarrow \text{C}_5\text{H}_{11} + \text{HCl}$ ," *J. Chem. Phys.* **109**(13) (1998) 5338.



# METATHESIS REACTIONS IN PENTANE AND PROPANE

## *Hydrogen-Abstraction Dynamics Probed with Synchrotron Radiation*



- **Chemical-reaction dynamics**
  - *Probes underlying mechanisms of chemical reactions*
  - *Strongly coupled experimental-theoretical effort*
  - *Detailed investigations of the forces between atoms, molecules that determine the chemistry*
  - *Provides the foundation for a predictive understanding of combustion and atmospheric chemistry*
- **Metathesis reactions**
  - *Atom-transfer from molecule to atom or radical*
  - *Simplest class of chemical reactions*
- **H-abstraction dynamics**
  - *Most common metathesis reaction*
  - *Broad importance in combustion*
  - *Important open questions*



# METATHESIS REACTIONS IN PENTANE AND PROPANE

## *Hydrogen-Abstraction Dynamics Probed with Synchrotron Radiation*



- **Reaction of Cl with pentane and propane**
  - *Prototypical H-abstraction reactions*
  - *Detailed insight into the chemical mechanisms of these reactions*
- **Key questions**
  - *Which H atom most important: primary, secondary, tertiary?*
  - *Where does the energy go?*
  - *Which product isomers are formed?*
  - *What are the underlying mechanisms?*
- **Crossed-beam studies using tunable VUV synchrotron radiation**
  - *Unique, universal, selective product detection*
  - *First-ever probe of the radical product yields a global view of the dynamics*
  - *Reveals detailed mechanisms, product identity, energy disposal*

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